

Glass Transition Temperatures of Polymers

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A. INTRODUCTION

Amorphous (noncrystalline) polymeric solids are either glasses or rubbers. A glassy polymer lacks long range order, and is below the temperature at which molecular motions take place on the time scale of the experiment. A rubbery polymer is above the temperature at which molecular motions take place on the time scale of the experiment. The glass transition temperature, T_g , is the critical temperature that separates glassy behavior from rubbery behavior. Many amorphous solids, including polymers, organic liquids, biomaterials, some metals and alloys, and inorganic oxide glasses, exhibit glass transition temperatures.

The dramatic change in the local movement of polymer chains at T_g leads to large changes in a host of physical properties. These properties include density, specific heat, mechanical modulus, mechanical energy absorption, dielectric coefficients, acoustical properties, viscosity, and the rate of gas or liquid diffusion through the polymer, to name a few. Any of these properties can be used, at least in a crude manner, to determine T_g .

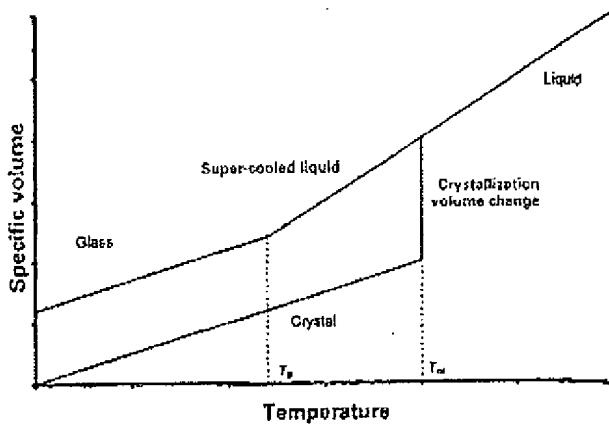


Figure 1.

1. Example of a Property Change at T_g

A classic method for determining T_g is dilatometry, in which the specific volume of the polymer is measured as a function of temperature. Figure 1 compares the specific volume vs. temperature curves for two idealized samples: a 100% amorphous material and a 100% crystalline material. Both materials follow the same path as their liquids are cooled from the melt. At the melting temperature, T_m , the crystallizing material orders into its crystal habit and exhibits a discontinuous decrease in specific volume. Below T_m , this solid has a reduction in specific volume with decreasing temperature, but the slope of this line, the volumetric thermal expansion coefficient, is less than the slope of the liquid line.

The amorphous material does not crystallize as the temperature falls below T_m , but continues to contract with a thermal expansion coefficient similar to the molten liquid; it acts as a supercooled liquid. At T_g , large-scale molecular motion (often considered to be the movement of 20–50 carbon atoms along a chain) becomes greatly reduced, the chain segments no longer rearrange rapidly in experimental time, and further cooling does not result in a similar volume change. Below T_g , the thermal expansion coefficient is similar to that of the crystalline solid. T_g can be defined as the temperature at the intersection of the two line segments. The specific volume is not discontinuous at T_g , as would be the case for the melting point, but the slope dV/dT is. Therefore, T_g is sometimes referred to as a second-order transition, as compared to the melting point, which is a first-order transition. Both the primary property, specific volume, and its differential, the volumetric thermal expansion coefficient, change at T_g and can be used to identify the event.

Most polymer samples are either completely amorphous or partially crystalline. Figure 2 shows the specific volume vs. temperature curve for a semicrystalline polymer. The crystallizable fraction becomes ordered as it cools to T_m . Below the melting point, the amorphous material continues to contract as though it were a supercooled liquid, while the crystalline portion has a smaller thermal

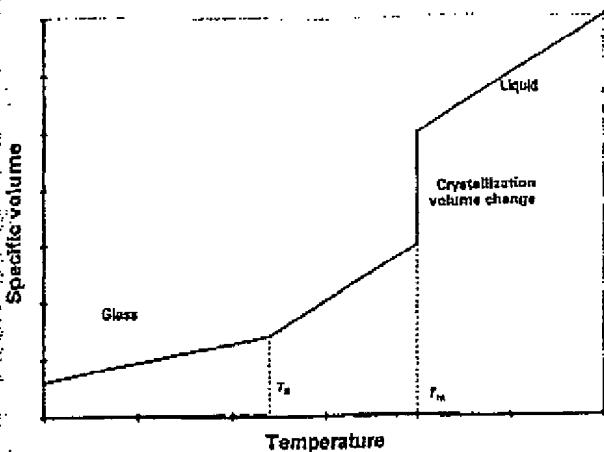


Figure 2.

expansion coefficient and contributes less to the volumetric decrease. Rapid amorphous phase motion stops at the glass transition temperature, and both solid components have similar thermal expansion coefficients below this temperature.

2. T_g: A "Non-Equilibrium" Transition

The glass transition temperature is not a fundamental thermodynamic property like the melting point because it is not thermodynamically stable, it is not defined by state variables, and its measurement is highly dependent on the time scale of the experiment used to determine its value. For example, experiments in which temperature or a deforming force is changed rapidly give higher T_g values than experiments in which conditions are changed slowly. Sample age and history affect the measurements as well.

The thermodynamic transition issue has been studied by a number of researchers. Staverman (1210) and Breuer and Rehage (1211) have concluded that T_g is not a true second-order transition because the glassy state is not completely defined by the normal state variables, p , V and T . Ehrenfest (1212) derived the following relationship that should hold for a true second-order transition:

$$\frac{dT_g}{dp} = \frac{T_g V(T_g) \Delta \alpha}{\Delta C_p} = \frac{\Delta \kappa}{\Delta \alpha}$$

where T_g is the glass transition temperature, p is the pressure, $V(T_g)$ is the molar volume at T_g, $\Delta \alpha$ is the thermal expansion coefficient difference (rubber to glass) at T_g, ΔC_p is the molar heat capacity difference, and $\Delta \kappa$ is the compressibility difference. Available data for a number of polymer systems show large deviations from the above equation for well-studied polymers, including polystyrene (1211), poly(isobutylene), poly(vinyl acetate), poly(vinyl chloride) and poly(methyl methacrylate) (1213,1214). The glass transition temperature is thought to be a kinetically controlled phenomenon (1215-1218).

B. T_g MEASUREMENT METHODS

The classical method of mercury dilatometer requires moderate amounts of sample, and time to permit thermal equilibrium to be achieved. Instruments that are easier to use and require only milligram quantities of sample are the thermal mechanical analyzer (TMA), the dynamic mechanical analyzer (DMA), and the differential scanning calorimeter (DSC). A TMA deforms a sample under a static load as the temperature is changed. At very low loads, it measures the specific volume change of the sample. A DMA measures the response of the material to an oscillating deformation. A DSC measures the change in sample enthalpy with time, dH/dt , for a known temperature program, dT/dt . The ratio of these two quantities gives dH/dT (also the specific heat capacity), which is a derivative measurement for T_g. (Experimental heat capacity curves of amorphous and semicrystalline polymers are given in the Heat Capacity chapter of this Handbook.) DSC is the most commonly used method for measuring the glass transition temperature of non-crosslinked polymers. All of these instruments can be interfaced to computers for data acquisition, test control, data reduction, and analysis.

The interpretation of T_g data can be controversial (1069-1071). The rate at which the sample is cooled or heated will affect the result. If the specific volume experiment of Fig. 2 was repeated for various cooling rates, T_g would occur at lower temperatures as the cooling rate is lowered, the transition region would become sharper, and a denser polymer would be produced. When a sample is allowed to remain below its glass transition temperature over a long period of time (aging), its density will increase. This process is called annealing; the rate of densification increases with annealing temperature.

1. Data Interpretation

The previous history of a sample will affect the measurement of T_g, unless the material's "memory" is erased by heating it well above the transition. The sample is heated well above its expected T_g, cooled to the original temperature, and reheated along a temperature profile to find the glass transition temperature of the material with minimal history. Some information can be inferred from the first heat, including residual stresses in the material, the presence of low-boiling diluents, etc.

The process of heating a polymer solid to find T_g often gives a curve similar to Fig. 1 and will produce a melt with the same density as that of the cooling experiment. However, in heating experiments, chain motions dominate the change in properties, and sudden property changes can occur near the transition temperature. At temperatures much higher than T_g, the property response once again becomes linear with temperature. In DSC measurements, sudden expansions can lead to an endothermic peak past the T_g. This endothermic peak has also been called enthalpy overshoot, and is thought to relate to the difference between the rate of temperature increase and the rate of increase of

chain mobility around T_g . The size of this overshoot depends on the annealing of the sample and the heating rate.

In a direct property measurement experiment (Fig. 1 is an example), it is common practice to ignore the kinetic effects of the transition region and to define T_g as the intersection of the two straight lines. For this case, the same T_g is found both on heating and cooling at a given polymer density. In an experiment that measures the differential of a property (DSC for example), integrating the curve gives the change in enthalpy from before to after the transition region, to which the simple intersection method of Fig. 1 can be applied, giving a T_g that is independent of heating rate (1079–1081). This method is well-known with inorganic glasses.

In DSC experiments, T_g is usually determined either by the onset point, the intersection of the initial straight line and the transition region straight line, or by the midpoint of the transition region (inflection point). The integration method's T_g is the same as the midpoint T_g if there is no endotherm, and is closer to the onset T_g if there is an endotherm. Moreover, it is common to measure T_g upon heating without any mention of previous thermal history or the heating rate. Because of these practices, the T_g values reported in this article should be considered as approximate by the reader. Authors reporting T_g should describe the thermal history of their measurements and also consider the integration method of determining T_g .

The classical methods of T_g measurement discussed previously can be quite insensitive for some polymers, e.g., highly crosslinked polymers. A penetration probe, on the other hand, is very sensitive and can determine T_g even on a thin film. But this method depends on the force of the penetrator and does not measure T_g in a fundamental way. Softening temperature methods are popular and are part of various ASTM standards.

2. Oscillating Load Methods

The measurement of the material response to an oscillating load gives a direct measure of the sample's modulus. The measurement of the lag of the material response (phase shift) to the mechanical forcing function gives a measure of the damping, or loss factor, of the sample. This last quantity is called the $\tan \delta$ peak value. Dielectric thermal analysis is done by using an oscillating electric field as the forcing function. At T_g , there is often an order of magnitude change in the modulus and a large maximum in $\tan \delta$. This α -transition is distinguished from other thermal transitions (β , γ , etc.) by being the most dominant and occurring at the highest temperature. An onset point, a midpoint, or a change in modulus by a certain amount have all been used to mark the glass transition temperature. The $\tan \delta$ maximum clearly specifies a thermal transition. However, it is necessary to independently determine that it is a glass transition and not another of the many transitions that appear in oscillating deformation methods. A classical T_g measured at a low programmed temperature rate (1 deg/

min) may correspond to a $\tan \delta$ measurement at a low frequency of measurement (1 Hz). The "loading rate" of a DMA experiment is the oscillating frequency, and T_g increases with frequency (analogous to the increase in T_g with heating rate in a DSC experiment). It is possible to measure a $\tan \delta$ maximum at constant temperature while the frequency is being scanned and there is an inverse relationship between temperature and frequency. Even at a reasonably low frequency (10 Hz), a $\tan \delta T_g$ can easily be 20–30°C greater than a classical one.

C. OTHER FACTORS AFFECTING T_g

Though the factors that govern T_g have been known for some years, there is still a wide variation in values for particular polymers. Polymer T_g 's are sensitive to parameters which may or may not have been evaluated by the authors. Published values should be reviewed considering all the factors which affect T_g . The main factors affecting T_g values are polymer structure, sample crystallinity, diluent types and concentrations, molecular weight distributions, previous thermal history of the sample, and system pressure. More detailed treatments are given in reviews (6,48,49,1241–1249).

1. Structure

Within families of similar polymers, increasing chain stiffness and interchain cohesion increase the glass transition temperature. Copolymers may have one or multiple T_g 's, depending on the ordering of monomers along the chain. The glass transition temperatures of copolymers may be higher, lower, or in between those of the homopolymers of their comonomers.

Most polymer structures are idealized and presumed from the characteristics of the reactants rather than proven by chemical and structural analysis. Structural uncertainties can arise both from the multiplicity of chemical reactions occurring during polymerization (especially those taken to high conversions), downstream processing, and from the structure of the reactants themselves. For example, a polymer with an asymmetric in-chain tetravalent atom can produce several stereoregular forms.

Alternatively, a polymer containing a residual double bond in the repeating unit could be in a *cis*, or *trans* conformation. Polymers of 1,3-dienes can have various combinations of *cis*, *trans*, 1,2- or 1,4-structures. Variations in these structural features can greatly effect the T_g values. Despite these uncertainties, the data are often useful if they can be regarded as pertaining to a polymer with reproducible properties.

2. Crystallinity/Crosslinking

Some workers suggest that the presence of crystallinity does not appreciably affect T_g . However, steric constraints imposed by crystalline regions on neighbouring amorphous polymer segments might result in an increase in T_g because

of the reduced mobility of these segments. In samples with crystallinity and moderate fractions of high molecular weight chains, tie molecules (long chains that have segments in more than one crystallite) provide physical crosslinking and increase T_g .

Some polymer families, such as the methacrylates and α -chloroacrylates, show high dependencies of T_g on tacticity. Intermolecular bonding can affect T_g either by increasing the cohesive energy of chain segments, or by decreasing the backbone degrees of freedom of chain segments. This last concept has been used (1240) to aid group contribution models.

As crystallinity increases, polymer T_g 's may be little affected (50), may increase (51,52) (at least for isothermal crystallization (53)) or may decrease (51,54). T_g values selected in this work are the highest quoted on the sample with the lowest degree of crystallinity, other factors being equal.

In general, the presence of crosslinks in a sample increases its T_g relative to an uncrosslinked sample. This effect can be independent of the chemical composition of the crosslinking agent, caused by the restricted motion of chain segments near crosslinking sites. However, the crosslinking agent can behave similarly to a second monomer, inducing either an increase or a decrease in T_g due to the copolymer effect.

3. Diluents

Much of the variation in published T_g data is caused by the use of impure samples. Common impurities are unpolymerized monomer, low molecular weight polymer, solvents, and water. Great care should be taken to remove such impurities. Their presence in small concentrations can lead to a shift (48,98–103) in T_g of over 40°C and sometimes the occurrence of "diluent transitions", for example "water peaks". Preferred values are from publications that describe the precautions taken to exclude diluents and the residual levels of these diluents. Few references contain this information and most values should be regarded as only provisional.

4. Molecular Weight

The T_g of a homopolymer generally increases with increasing molecular weight up to a limiting value, known as the limiting or persistent T_g value (48,104,105). The reverse may hold for polymers with particular end-groups (106), or where crystallinity decreases with increasing molecular weight (107). For some polymers, T_g 's are independent of molecular weight (108).

Many data, especially on condensation polymers, are for polymers of rather low molecular weight and it seems likely that higher T_g values would be obtained if higher molecular weight samples were tested. Many polymers are not properly characterized with respect to molecular weight and few have reported molecular weight distributions. In many cases, the only measure of molecular weight is a

viscosity value, which itself can be very dependent on solvent–polymer interactions and, to some extent on the temperature. Usually, the highest viscosities and the highest molecular weight polymers are associated with the most reliable data.

The classical model for the effect of molecular weight on T_g is (1219–1226)

$$T_g = T_g^\infty - \frac{A}{M_n}$$

This model suggests that the glass transition temperature reaches a limiting value when the number average molecular weight of the polymer is large. Cowie and Toporowski (1220) have shown that there is no further increase in T_g when the molecular weight is above a critical value, which is similar to the critical molecular weight for viscosity.

5. Thermal History

We have previously discussed in detail how thermal history (cooling rate, annealing time, and temperature), as well as the method of T_g measurement affects the reported T_g .

6. Pressure

Increasing pressure increases T_g in a linear relationship. A simple model is (Refs. 1227–1230)

$$T_g(p) = T_g(0) + sp$$

where $T_g(p)$ is the glass transition temperature as a function of pressure, p is pressure, and s is the linear pressure coefficient. This coefficient is 0.2 K/MPa for flexible aliphatic chains, and 0.55 K/MPa for semirigid aromatic chains (1231–1233). The effect of pressure on T_g can be important in some processing applications, such as injection molding. A different method for modeling the effect of temperature takes into account pVT data near T_g (1235–1237), giving an equation that includes the bulk modulus of the polymer glass.

D. ESTIMATION METHODS FOR THE GLASS TRANSITION TEMPERATURE

Several researchers have developed group contribution methods for correlating polymer properties, including the glass transition temperature (1238–1240). These techniques emphasize quantitative modeling of the various effects of polymer structure on T_g , and are a valuable aid to interpreting experimental data and estimating glass transition temperatures for new materials.

E. CLASSIFICATION, NOMENCLATURE, AND ABBREVIATIONS

Over 10000 papers contain glass transition data (43). This section of *Polymer Handbook* represents a fraction of these

data. Most of the data in the tables are for linear homopolymers. In general, the polymers contain no additives or diluents, and are thought to have low or no branching.

Polymers are subdivided into principle classes by the composition of their repeating chain segment: acyclic carbon polymers, carbocyclic polymers, acyclic heteroatom polymers, heterocyclic polymers, and copolymers. All entries are placed in the most senior class their structure commands (109,110) and appear in only one class. The subclasses and their entries are organized in alphabetical order.

1. Naming Conventions

With the exception of common polymers with accepted trivial names, the polymers are named substantially according to the ACS recommendations for polymer nomenclature (110) in conjunction with IUPAC rules (109); less common polymers are cross-referenced from the trivial to the systematic name. Systematic names are not given for all the polymers in order to save space. Substitutive nomenclature is generally used for simple radicals, but for long combinations of radicals replacement nomenclature has been used to provide a much shorter name (as for some fluorocrylates with other side chains).

When sequences of radicals have repeated, the repeating sequence has been written once and prefixed "di", "tri", etc. as appropriate, for example, di(oxyethylene) for the sequence $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$. Note that the diradical "di(oxyethylene)" must be distinguished from the diradical "dioxyethylene" which has the structure, $-\text{O}-\text{O}-\text{CH}_2-\text{CH}_2-$, and also the diradical "ethylenedioxy" which has the structure, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ (IUPAC rule C205.2). The principle underlying the last-named diradical has not generally been extended to the naming of polymers in this section, i.e., diradicals of structure $-\text{X}-\text{Y}-\text{X}-$ are not named YdiX , with the exception of alkanedioyl diradicals, because of the difficulty of locating indexed polymer names in which the diradicals are not named from left to right. Many polymers are derivatives of the diradical "propylene" $-\text{CH}(\text{CH}_3)-\text{CH}_2-$; the substituted diradical

"propylene" is used in naming polymers instead of "1-methylethylene" which could be preferred.

Polymer names are tabulated in alphabetical order within each subsection, but

1. prefixes like *sec-*, *tert-*, including designated atoms and the numbers showing locations of substituents are ignored except as secondary and tertiary indicators of order. For example, poly(ethylene 2,6-naphthalate) appears before poly(ethylene 1,4-terephthalate); poly(4-*p*-anisoylstyrene) appears before poly(4-benzoylstyrene).
2. multiplying prefixes for various substituents, such as dimethyl or trimethyl, are observed in alphabetical ordering rather than being grouped together as in the 3rd edition of this Handbook.
3. the locations of substituents in otherwise identical polymers are taken as tertiary indicators of order: the numbers are arranged in increasing order at the first point of difference. Thus, 2,3,8- comes before 2,4,1-.

Comments may include information as to the instrument of measurement and, whenever possible, information regarding the method of DSC measurement (e.g., onset), conditions of measurement, thermal history, and whether measurements were made as a function of a particular variable such as molecular weight ($f(MW)$).

2. Abbreviations

HR	Heating rate
CR	Cooling rate
0CR	Zero cooling rate
Xp	Extrapolate
TH	Thermal history
DSC	Differential scanning calorimeter
TMA	Thermal mechanical analyzer
DTA	Differential thermal analysis
DMA	Dynamic mechanical analyzer
MW	Molecular weight
$f(MW)$	Function of a variable
Mdpt	Midpoint
Intg	Integration

F. TABLES OF GLASS TRANSITION TEMPERATURES OF POLYMERS

TABLE 1. MAIN-CHAIN ACYCLIC CARBON POLYMERS

Polymer	CAS No.	T_g (K)	Remarks	Refs.
1.1. POLY(ACRYLICS) AND POLY(METHACRYLICS)				
1.1.1. POLY(ACRYLIC ACID) AND POLY(ACRYLIC ACID ESTERS)				
Poly(acrylic acid)	9003-01-4	379 348		720,811-818 1293
Poly(1-adamantyl acrylate)		426		1401,1349
Poly(adamantyl crotonate)		507		1349
Poly(adamantyl sorbate)		388		1349
Poly(benzyl acrylate)		279		746,1447